Synthesis of fatty alcohol mixtures from oleochemicals in supercritical fluids†

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Hydrogenation of various types of oleochemicals is a major unit operation in industry. Traditional methods utilize batch, stirred reactor operation resulting in long reaction times and excessive use of catalyst and hydrogen. In this study, reduction of fatty acid methyl esters (FAME) to fatty alcohol mixtures in two different types of supercritical media (H_2/CO_2 and H_2/C_3H_8) were compared using two different hydrogenation catalysts. High and rapid conversions are achieved at the highest experimental temperature (250 °C) and at a hydrogenation mole fraction of 0.25. The described hydrogenation methods has been coupled with an enzymatic-catalyzed transesterification to yield a novel sequential two step synthetic procedure, which permits high fatty alcohol yields to be achieved directly from soybean oil.

Introduction

Fatty alcohols and their derivatives are important in many industrial processes where they are used as raw materials for surfactants and lubricants. A fatty alcohol is, in general defined as a monohydric aliphatic alcohol with six or more carbon atoms. The annual production of fatty alcohols is over 1 million metric tons. Commercially, fatty alcohols are produced by one of three processes: the Ziegler process, the Oxo process or by a high pressure hydrogenation of fatty acids or esters. The latter process is the only process that uses natural fats or oils whereas the two first processes utilize petrochemical feedstocks.[1] Depending on their application, fatty alcohols are divided into subgroups. Thus fatty alcohols having eleven or more carbon atoms are usually called detergent range alcohols because they are used in the detergent industry mainly as sulfate, ethoxylate or ethoxy sulfate derivatives. Fatty alcohols with less than eleven carbon atoms are called plasticizer range alcohols, and they are used as plasticizers and lubricants mainly in the form of ester derivatives.

The conversion of many lipid species to other useful oleochemical compounds can be readily accomplished in supercritical carbon dioxide (sc-CO_2). This is due to the relatively high solubility and diffusivity of these compounds in dense CO_2. Further, the strong pressure dependence of reaction rate constants promotes exact control of the reactions. A large number of chemical reactions have been successfully conducted in supercritical fluids,[2–7] including hydrogenation[8–11] and lipase-based catalysis of oils/fats.[12,13] Further, esterifications, glycerolyses, and hydrolyses of vegetable oils have been performed in sc-CO_2. In addition, hydrolyses of fats/oils can be achieved using subcritical water.[14]

Recently Harrod *et al.*[15–17] and Tacke and co-workers[18,19] have explored the hydrogenation of oleochemicals. These investigators have provided convincing evidence that hydrogenation of fats/oils and oleochemicals is feasible under supercritical conditions, using agents as sc-CO_2 and supercritical propane (sc-C_3H_8). Patents[20,21] have been submitted/issued, claiming the uniqueness of the above processes, although the economic rationale and willingness of industry to accept these unusual approaches is still unknown. Moreover, somewhat unconventional catalysts, as compared to those currently used in industry, were used to perform the hydrogenation in small-scale flow reactors.

In this study, we have extensively investigated the hydrogenation of fatty acid methylesters (FAMES) of soybean oil using mixtures of hydrogen with sc-CO_2 or sc-C_3H_8. A novel experimental approach has been developed using commercially available supercritical fluid extraction (SFE) instrumentation, and the reaction conditions have been optimized for a flow reactor. The derived product mixtures have been characterized using gas chromatography (GC) as well as capillary supercritical fluid chromatography (SFC); the results indicate that

Green Context

This paper demonstrates the feasibility of the continuous hydrogenation of fatty acid methyl esters from vegetable oil resources using a 'green' synthesis approach. The new route is based on supercritical carbon dioxide as an environmentally benign solvent, a lipase catalyst and a chromium-free catalyst for the hydrogenation step. One of the products from the hydrogenation step is methanol and this can be recycled back to the transesterification step. The integration of several cleaner and safer technologies will become increasingly important in future process chemistry. The fatty alcohol mixtures from the above synthesis are potential feedstocks for the industrial synthesis of surfactants or they could be fractionated further to produce higher purity oleophilic alcohols. *JHC*

† Names are necessary to report factually on available data; however the U.S. Department of Agriculture (USDA) neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may be suitable.

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there are advantages and disadvantages of the use of either the sc-H_2/CO_2 or the sc-H_2/C_3H_8 systems. High yields of saturated alcohols are realized (*ca.* 90% steryl alcohol) at pressures and temperatures above 150 bar and 210 °C, respectively. The reaction utilizes conventional hydrogenation catalysts and has been successfully coupled with enzymatic synthesis of the FAMES in sc-CO_2 to yield a two step, highly efficient reaction sequence for converting vegetable oils to saturated alcohol mixtures.

Experimental

The basic experimental apparatus for studying the hydrogenation of FAMES under supercritical conditions is shown in Fig. 1 The individual gases (fluids) were metered using a Brooks Series 5850E mass flow controller, whose output was fed into a 1000 mL capacity Parr Instruments Co. high pressure, stirred autoclave (Model No. 4501 Parr Instruments Co., Moline, IL) to assure homogeneity. The resultant binary fluid mixture was then compressed to the desired reaction pressure using a Haskel AGT-62/152 gas booster compressor (Haskel Mfg. Co., Burbank, CA) and introduced into the reaction vessel containing either copper chromite catalyst E-406TU (Engelhard Inc., Erie, PA) or a chromium-free catalyst, T-4489 (United Catalysts Inc., Louisville, KY). For the determination of the void volume of the filled reaction cell, the cell was connected to a supercritical fluid chromatograph; void volume was achieved on injection of carbon tetrachloride. For the reactions, the cell was contained in the thermostatted oven of a Speed supercritical fluid extraction unit (Applied Separations Inc., Allentown, PA). The synthesized alcohols were collected in a vial after

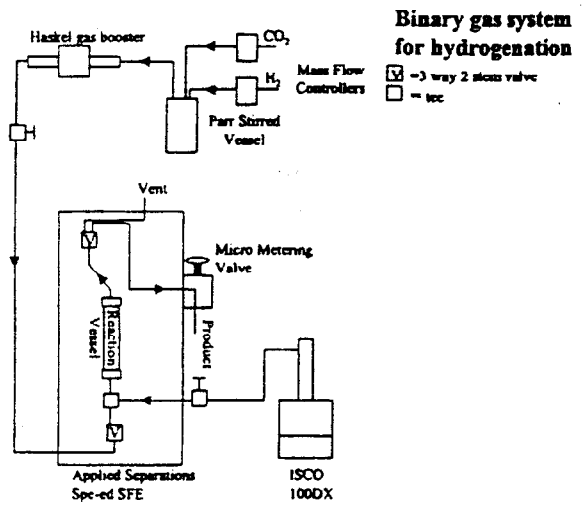

Fig. 1 Reaction system for hydrogenating FAMES to alcohols using binary fluid mixtures of sc-H_2/CO_2 or sc-H_2/C_3H_8.

decompression of the binary fluid mixture through the micro metering valves on the Speed unit. The expanded gas was measured with a gas flow meter. The byproduct methanol was trapped in a condenser. The mass balance was not validated, however, any unconverted methyl esters would show up in the subsequent GC or SFC analysis.

As shown in Fig. 1, the FAME feedstock was fed into the sc-H_2/CO_2 or sc-H_2/C_3H_8 stream using an Isco Model 100 DX syringe pump (Isco, Inc., Lincoln, NE). The FAME-sc-H_2/CO_2 or sc-H_2/C_3H_8 mixture was then transported over the hydrogenation catalyst contained in one of several small volume reactor vessels (1–4.5 mL cells). For these experiments, a variety of Isco syringe pumps were utilized to deliver reagents (soybean oil, methanol, FAMES) as well as liquefied fluid (CO_2). For the initial hydrogenation studies, a welding-grade CO_2 was used in conjunction with hydrogen Grade 4 (The BOC Group Inc., Murray Hill, NJ) or propane from the same source. In later experiments involving enzymatic synthesis of FAMES, SFC/SFE-Grade CO_2 (Air Products and Chemicals Inc., Allentown, PA) was used and delivered *via* a cooled syringe pump. Soybean oil (refined, bleached, and deodorized) was obtained from Riceland Industries; and the FAME feedstock with the exception of the enzymatically-synthesized product, from either Chemol Company (Chemol Company Inc., Greensboro, NC) or SoyGold 1100 (AG Environmental Products L.L.C., Lenexa, KS).

The system used to study the sequential, two-step reaction conversion of soybean oil to fatty alcohol mixtures coupled an Isco SFX-2-10 extractor module with flanking Isco syringe pumps that were used to deliver the oil, 4 μL min^{-1}, and methanol, 5 μL min^{-1}, respectively into the sc-CO_2 prior to the reactor cell. Transesterification of soybean oil was accomplished using a similar procedure and conditions as described by Jackson and King.[22] Utilizing a pressure of 170 bar and a temperature of 50 °C, a supported enzyme catalyst, isolated from *Candida Antarctica*, Novozym SP 435 (Danbury, CT) contained in a 2.5 mL reaction vessel, was employed as a small tubular reactor for the oil to FAME conversion. The resultant product was then transferred into the apparatus shown in Fig. 1 using sc-H_2/CO_2 to hydrogenate the synthesized FAMES.

Gas chromatographic analysis of the resultant fatty alcohols or by-products, and the starting reactants (FAMES), utilized a HP-1 25 m, 250 μm i.d., 0.25 μm film thickness column contained in a Hewlett Packard Model 6890 gas chromatograph (Little Fall, PA). The supercritical fluid chromatographic (SFC) analysis of product/reactant mixtures from the enzyme synthesis step was accomplished using a Dionex Series 600 SFC (Dionex Inc., Salt Lake City, UT) containing a SB-Methyl-100, 10 m, 50 μm i.d., 0.25 μm film thickness column (Dionex Inc., Salt Lake City).[23]

The experimental parameters that were investigated in this study are listed in Table 1. Both types of hydrogenation catalysts were tested with the sc-H_2/CO_2 and sc-H_2/C_3H_8 mixtures over a pressure range of 150–250 bar and a temperature range of 210–250 °C. Here all solvents are above their critical points. The mole fraction of hydrogen in the sc-CO_2 and sc-C_3H_8 ranged from 0.10–0.25. Residence times in the reactor vessels ranged from 4–9 s, while FAME feed for the

Table 1 Range of experimental conditions investigated utilizing the system in Fig. 1 for hydrogenation of FAMES to alcohols

Fluid	Catalyst	*P*/bar	*T*/°C	Mole fraction (H_2)	Residence time/s	Substrate flow/μL min^{-1}
CO_2	Copper chromite	150–250	210–250	0.10–0.25	4–9	25–50
CO_2	Chromium free	150–250	210–250	0.10–0.25	4–9	25–50
Propane	Copper chromite	150–250	210–250	0.10–0.25	4–9	50–250
Propane	Chromium free	150–250	210–250	0.10–0.25	4–9	50–250

sc-H_2/CO_2 system was 25–50 and 50–250 μL min^{-1} for the sc-H_2/C_3H_8 mixtures. Critical parameters and densities were calculated using Isco SF Solver program (Isco).

The experiments were done in a 2^{5-1} factorial design including four center points resulting in a total of 20 experiments. In a typical run, after 20 min temperature equilibration using a continuous gas flow, the substrate pump was started and allowed to run an additional 20 min. Finally a sample was collected during a 20 min period. The evaluation of the optimum reaction conditions was made by using Codex (Sum-it System, Solna, Sweden).

Results and discussion

Scouting experiments showed that incomplete reaction only resulted in saturation of the double bonds of the fatty acid chain together with the production of a small amount of fatty alcohols. When the reaction, on the other hand, was allowed to go too far, extensive *n*-alkane formation resulted.

For the sc-H_2/CO_2 as well as for the sc-H_2/C_3H_8 system only two of the variables were found to have a significant impact on the hydrogenated product purity. These were temperature and hydrogen content of the fluid. These variables should be kept at a high level, as is clearly evident from the response surfaces shown in Figs. 2(*a*) and (*b*). The substrate flow rate, pressure and residence time were not found to have a significant effect on the hydrogenation process in the investigated experimental domain. As an example, a response plot obtained with the chromium free catalyst and sc-H_2/C_3H_8 mixtures is shown in Fig. 2(*b*). When the hydrogenation was performed under optimal conditions the two catalysts gave similar results. The catalyst was used multiple times.

The response surface for the sc-H_2/C_3H_8 system indicates that high alcohol conversions can be accomplished also when using lower mole fractions of hydrogen in propane than for the corresponding sc-H_2/CO_2 system (*ca.* 50%). Response surfaces for the copper chromite catalyst, Figs. 2(*c*) and (*d*), follow a similar pattern but the trends are not as clear. At high mole fractions of H_2 the sc-H_2/CO_2 system is superior to the sc-H_2/C_3H_8 system. However, at low mole fractions of H_2, both the sc-H_2/CO_2 and the sc-H_2/C_3H_8 systems give approximately the same yield, *i.e.*, 80% conversion. This indicates the importance of catalyst selection for the overall yield and the reaction conditions that are required.

The gas chromatographic profiles of the hydrogenated product mixtures derived from the reaction in the sc-H_2/CO_2 and sc-H_2/C_3H_8 systems are shown in Figs. 3(*a*) and (*b*). Peaks were tentatively identified by comparisons with the retention time of standard compounds. In Fig. 3(*a*), the flame ionization detector (FID) response indicates a high degree of conversion yield (97.2%) for both methods used to prepare the hydrogenated fatty alcohols (steryl and palmityl alcohols) from soybean oil. Only trace levels of unconverted FAMES remain. However, Fig. 3(*b*) which shows the composition of the product obtained with the sc-H_2/C_3H_8 system, indicates not only the appearance of the fatty alcohols, but also significant amounts of C_{16} and C_{18} *n*-alkanes as by-products. This has been observed also by other researchers.[23,24] In this case, the two alcohols constitute 95% of the product, while the *n*-alkane components were 4.6% of the total product yield. Both product mixtures were generated at 250 bar, 250 °C, a hydrogen mole fraction of 0.25 and a residence time of 9 s, using chromium-free catalyst.

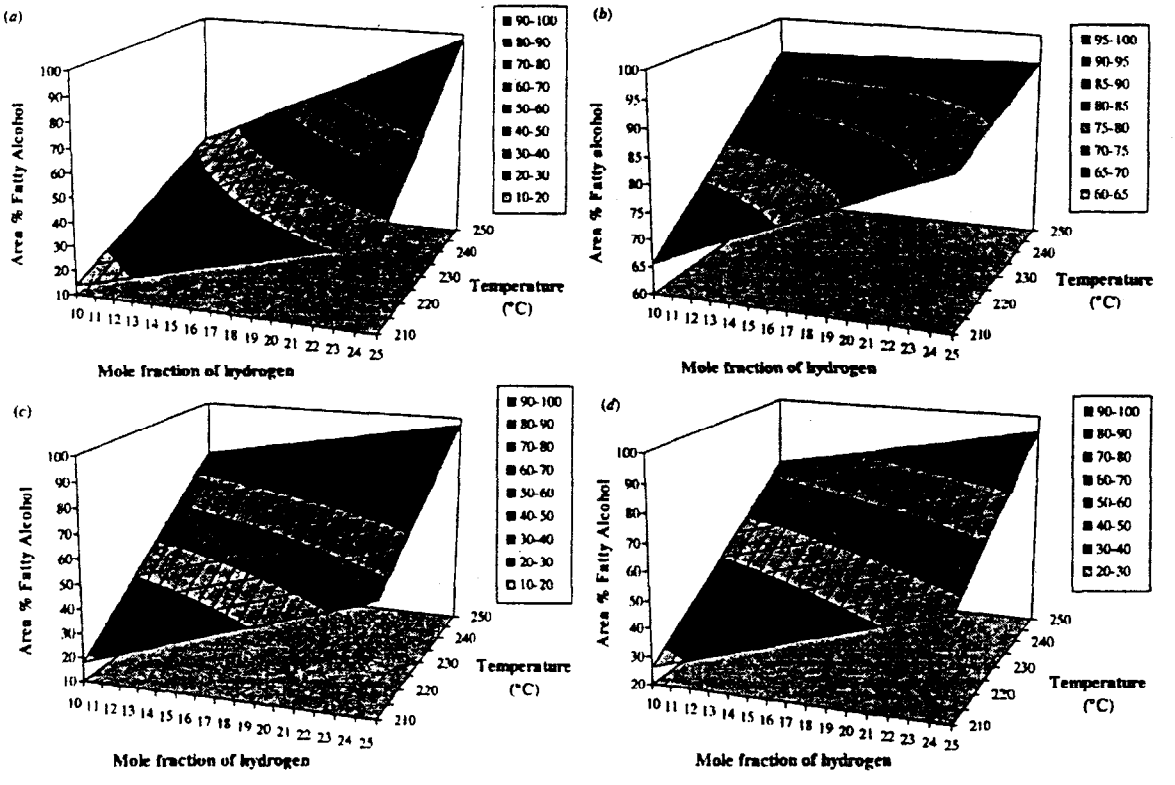

Fig. 2 (*a*) Response surface plot for production of fatty alcohols using chromium-free catalyst in sc-H_2/CO_2. Approximate residence time, 5.5 s; substrate flow, 37.5 μL min^{-1}; pressure, 200 bar. (*b*) Response surface plot for production of fatty alcohols using chromium-free catalyst in sc-H_2/C_3H_8. Approximate residence time, 5.5 s; substrate flow, 150 μL min^{-1}; pressure, 200 bar. (*c*) Response surface plot for production of fatty alcohols using copper chromite catalyst in sc-H_2/CO_2. Approximate residence time, substrate flow and pressure as in Fig. 2(*a*). (*d*) Response surface plot for production of fatty alcohols using copper chromite catalyst in sc-H_2/C_3H_8. Residence time, substrate flow and pressure as in Fig. 2(*b*).

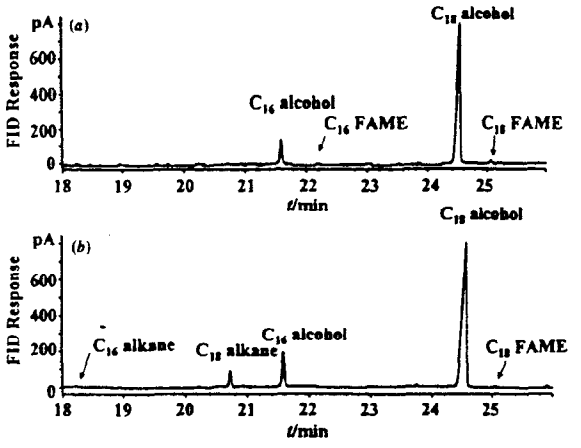

Fig. 3 (*a*) GC profile of products from critical fluid hydrogenation (sc-H_2/CO_2) of FAMES using chromium-free catalyst. Reaction conditions: pressure 250 bar, temperature 250 °C, mole fraction of H_2 0.25, residence time 9 s; substrate flow rate 50 μL min^{-1}. (*b*) GC profile of products from critical fluid hydrogenation (sc-H_2/C_3H_8) of FAMES using chromium-free catalyst. Reaction conditions: pressure 250 bar, temperature 250 C, mole fraction H_2 0.25, residence time, 9 s; substrate flow rate 250 μL min^{-1}.

Using copper chromite catalyst for the two binary gas mixtures under basically the same conditions yielded a similar result.

Thus there are tradeoffs in employing the sc-H_2/CO_2 or sc-H_2/C_3H_8 system; the first system allows the highest potential conversion to alcohols to be achieved, while the second binary fluid mixture (H_2/C_3H_8) permits a higher throughput. The rate of conversion of FAMES to alcohols is higher for the sc-H_2/C_3H_8 mixture than for the sc-H_2/CO_2 binary fluid. For example, 3 times more alcohol can be synthesized in the sc-H_2/C_3H_8 mixture in 2/3 of the time as compared to what can be accomplished under similar conditions in the sc-H_2/CO_2 system.

Fig. 4 illustrates the GC product mixture obtained when using enzymatic catalysis to form the FAMES from soybean oil followed by a hydrogenation over a chromium-free catalyst. This was accomplished using the complex system shown in Fig. 5. Here the hydrogenation step uses the identical experimental apparatus previously noted for the critical fluid hydrogenations (Fig. 1). A multiple syringe pump system (A–D) was used to deliver the appropriate amounts of CO_2 (A–B), soybean oil (C), and methanol (D) into the extraction (reaction) cell of an Isco SFX-2-10 module (E), containing the Novozym SP 435 catalyst. The resultant product from the transesterification (Fig. 4) was then fed into the flow stream as designated in the hydrogenation sequence of the overall reaction. High conversion to alcohols, 96.5% yield, with only traces of the original FAMES and *n*-alkanes were detected in the chromatogram (Fig. 4). This demonstrates that the two-stage reaction sequence performs well when using the same conditions as applied for the

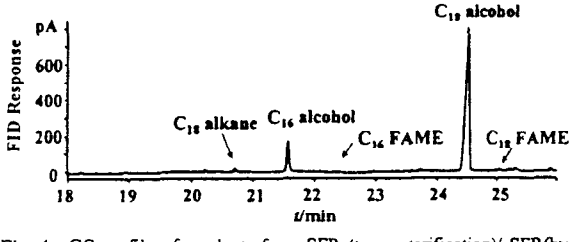

Fig. 4 GC profile of products from SFR (transesterification)/ SFR(hydrogenation-sc-H_2/CO_2) of soybean oil. Reaction conditions for the transesterification step: pressure 170 bar, temperature 50 °C; oil flow rate 4 μL min^{-1}, methanol flow rate 5 μL min^{-1} CO_2 flow rate 1 mL min^{-1}. Reaction conditions for the hydrogenation step: pressure 250 bar, temperature 230 °C, mole fraction of H_2 0.25, residence time 9 s.

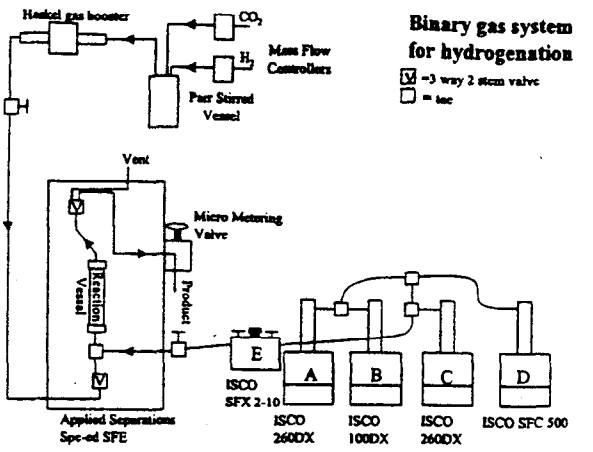

Fig. 5 Reaction system for performing transesterification of soybean to FAMES followed by critical fluid hydrogenation reaction to produce fatty alcohol mixtures.

reactions leading to the product composition in Fig. 3(*a*). The conversion of the soybean oil over Novozym SP 435 was examined using capillary SFC. The reaction was relatively complete; C_{16}, C_{18} FAME and only minor amounts of mono-, di- and tri-glyceride appeared in the chromatogram as shown in Fig. 6.

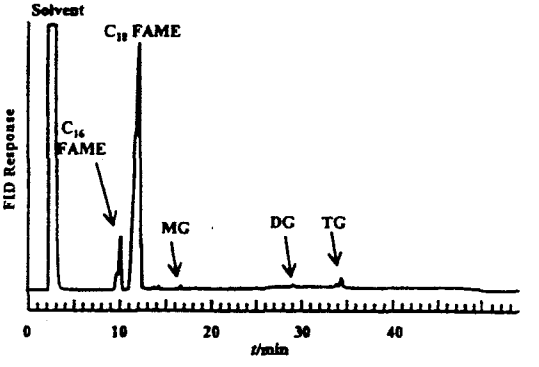

Fig. 6 SFC profile of the transesterification step using Novozym SP 435. MG, mono-glyceride; DG, di-glyceride; TG, tri-glyceride.

Conclusions

Reaction in supercritical propane resulted in the highest production of fatty alcohol per time unit. However, when using propane, significant amounts of C_{16} and C_{18} *n*-alkane were formed as by-products while virtually no alkanes were formed in carbon dioxide, which is a distinctive advantage. Further, carbon dioxide is more environmental compatible and non-flammable. Moreover, the enzymatic catalysis followed by hydrogenation gave a high yield, only traces of FAME and alkanes were present in the product. The results in this study demonstrate the feasibility of continuous hydrogenation of fatty acid methyl esters from vegetable oil resources using a 'green' synthesis approach.

Our study was accomplished using analytical scale equipment and such 'green' reagents as carbon dioxide, a lipase catalyst, and a chromium-free catalyst for the hydrogenation step. For the hydrogenation step, the rapid conversion rate of the FAME substrate suggests a potentially high production rate if the process is scaled up. It is interesting to note that these 'supercritical' hydrogenations are dependent on the choice of catalyst with respect to optimization of product yield and

distribution. Since one of the products from the hydrogenation step is methanol, there is a possibility to recycle this alcohol back to the transesterification step to be utilized as a reactant for forming more FAMES.

FAMES as opposed to neat fatty acids should be viewed as a key synthetic starting material for the synthesis of oleochemicals in critical fluid media. This is because they minimize corrosion of reactor materials and attrition of the catalyst. The resultant fatty alcohol mixtures from the above reaction sequence are potential feedstock for industrial synthesis of surfactants.[25] In addition, they could be fractionated further, perhaps using supercritical fluid fractionation, to produce even higher purity oleophilic alcohols.

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